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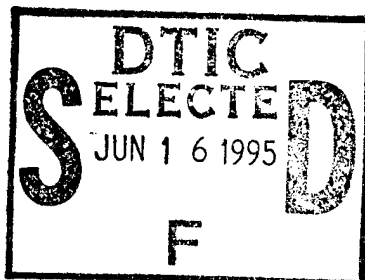


The Relationship of Chemical Structure to Supercritical-Fluid Solubility and to Cosolvent-Modifier Properties: A Literature Review

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| 13. ABSTRACT (Maximum 200 words) <p>This report describes a literature review on solubility and cosolvent effects in supercritical fluid extraction (SFE). A cosolvent modifier is a second solvent that is added, usually in small (<10%) amounts, to a supercritical solvent to enhance the solubility of a solute in that solvent. In general, nonpolar solvents such as ethane tend to most efficiently dissolve nonpolar solutes such as hydrocarbons, while more polar solvents such as CHF₃ tend to most efficiently dissolve more polar solutes. Supercritical carbon dioxide (SF-CO₂) is a fairly good general solvent. With regard to cosolvent effects, the main correlation seems to be that in order for addition of a given cosolvent to cause a large increase in the solubility of a given solute, there should be a specific interaction (e.g., hydrogen bonding, charge transfer, dipole-dipole interaction, etc.) between the solute and the cosolvent involved. The behavior of HMX and RDX in supercritical fluid chromatography (SFC) and SFE behavior are also summarized. Finally, some suggestions are made as to possible ways of enhancing the extractability of HMX and RDX in supercritical solvents.</p> <p style="text-align: right;">DTIC QUALITY INSPECTED 3</p> | | | | |
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1. INTRODUCTION

There is considerable current interest in the disposal of excess or waste propellants and explosives, preferably with recovery of the ingredients. One method under consideration is supercritical fluid extraction (SFE); this would involve treating the waste material with a supercritical solvent, namely, a solvent whose temperature and pressure are such as to place it above its critical point (i.e., the temperature and pressure above which the distinction between the gas and liquid states disappears). Solvents in this condition have useful properties due to the fact that their densities, and hence other properties as well, including solubility, can be varied over a much larger range than is the case for normal liquids. In addition, supercritical fluids (SFs) have lower surface tension and viscosity than normal liquid solvents, and the resulting improved ability to penetrate cracks and surface pores results in increased dissolving and extracting power.

The propellants (and explosives) in question contain about 75% nitramine (HMX or RDX) as an oxidizer; the remainder of the propellant is mainly polymeric binder, as well as small-molecule additives such as stabilizers and plasticizers. Since the crystalline nitramine oxidizer is the major component, the most important problem is to find an extractant capable of dissolving this nitramine. The most promising candidate SF solvents are CO_2 , N_2O , NH_3 , CH_3F , and CHF_3 ; of these, CO_2 is the most interesting because it is inexpensive, easily available, and environmentally innocuous. Unfortunately, HMX and RDX have only limited solubility in supercritical CO_2 (SF- CO_2); therefore, the use of cosolvent modifiers to enhance their solubility is being investigated. A cosolvent modifier is a compound which, when added to an SF solvent, increases the solubility of solute molecules in that solvent. Typical cosolvent modifiers include methanol, acetone, and acetonitrile; others will be discussed in subsequent text.

The objective of this report is to review (a) existing data on relationships between the chemical structure of solute molecules and their solubility in SF- CO_2 ; and (b) existing data on relationships between the structure of molecules and their ability, when used as cosolvent modifiers, to enhance the dissolving power of SF- CO_2 toward organic solutes. It is expected that the results of this review will be useful in identifying solvents and modifiers for SF extraction of components from excess gun propellants and explosives. The compounds of immediate interest are, as mentioned above, HMX and RDX; therefore an attempt will also be made to review available information on SFE, SF solubility, and supercritical fluid chromatography (SFC) of HMX and RDX. An attempt has been made to achieve complete coverage through approximately mid-1993; some later references are also included.

Paulitis et al. (1983) and Bartle et al. (1991) have tabulated existing experimental studies on solubilities in supercritical-fluid CO₂ (SF-CO₂), but made few comments on structure-solubility relationships. Johnston et al. (1989) have summarized some theoretical and experimental studies on supercritical solubility and solubilization. Sato (1987) and Arai and Iwai (1988) have also published reviews of SFE cosolvent effects, however, they are in Japanese and have not yet been translated into English. Sunol, Hagh, and Chen (1985) discussed cosolvent modifier or "entrainer" selection, including the importance of hydrogen bonding; they also described a supercritical extraction system which they used for evaluation cosolvent modifiers. The reader is also referred to Chester, Pinkston, and Raynie (1992).

The present review will be concerned primarily with SFE and with the use of cosolvent modifiers therein, although where appropriate some reference will also be made to the use of cosolvent modifiers in SFC. Related techniques such as gas antisolvent recrystallization (Gallagher et al. 1992; Naufflett and Farncomb 1992) and supercritical water oxidation (Buelow et al. 1992; Brill 1992) will not be considered explicitly in the body of this review.

2. SFE AND SFC STUDIES ON HMX AND RDX

Since current efforts in this laboratory (Morris et al. 1993) are focused on identifying an appropriate supercritical solvent for HMX and RDX, it seems appropriate to begin by reviewing existing literature describing SF behavior of these compounds.

Liebman and Griff (1991) studied the SFE of HMX and RDX and propellants containing them. They found that it was very difficult to extract HMX and RDX with unmodified SF-CO₂, but that HMX could be extracted with the use of cosolvent modifiers; the best modifiers tested were acetonitrile, acetone and methanol. For example, reasonable results were obtained with SF-CO₂ modified with 4% acetonitrile. Because of the generally greater solubility of RDX, it was assumed that RDX would also be extractable under these conditions.

Morris et al. (1993) described studies of the SFE of RDX and of some propellants containing RDX. This was a progress report on a recently initiated project. It was found that RDX appeared to be measurably, but only very slightly, soluble in unmodified SF-CO₂, but that use of acetonitrile or nitromethane as cosolvent modifiers gave, respectively, a 93-fold and a 53-fold increase over neat SF-CO₂ with regard to the amount of RDX extracted, while methanol gave about a 7-fold increase. Isopropanol

gave only a 1.5-fold increase. (These results are summarized in Table 1.) It was pointed out that since a dynamic (flowing) rather than a static (stopped-flow) SFE method was used, these results may well indicate increases in kinetic rates of dissolution rather than true enhancements in thermodynamic solubility. More recent results (Morris et al. 1994a) suggest that γ -butyrolactone and N,N-dimethylformamide may be even better cosolvents than are acetonitrile and nitromethane.

Table 1. Relative Modifier Efficiency in SFE of RDX^{a,b}

| Modifier | Relative RDX Peak Area | Dipole Moment (D) ^c |
|----------------------|------------------------|--------------------------------|
| Acetonitrile | 93.0 | 2.87 |
| Nitromethane | 52.7 | 3.46 |
| Methanol | 6.6 | 1.69 |
| Isopropanol | 1.5 | 1.69 |
| Neat CO ₂ | 1.0 | — |
| Water | 0.7 | 1.85 ^d |

^aPressure 55 MPa, Temperature 55° C.

^bMorris et al. (1993).

^cDean (1987).

^dWeast (1968).

Studies (Morris et al. 1994a, 1994b, to be published) on low-vulnerability artillery (LOVA) propellant using unmodified SF-CO₂ and SF-CO₂ modified with acetonitrile indicated that less RDX was extracted than expected on the basis of studies on pure RDX; this was especially noticeable in the case of the acetonitrile-modified SF-CO₂, which also caused swelling and softening of the propellant grain. These studies have continued.

Slack, McNair, and Wasserzug (1992) reported SFE of RDX from Semtex (a plastic explosive consisting of RDX in a matrix of styrene-butadiene copolymer and hydrocarbon oil) with SF-CO₂. No solubility or extraction data, use of cosolvent modifiers, or difficulties with RDX extraction were mentioned.

Douse (1988) and Griest, Guzman, and Dekker (1989) reported SFC on a variety of explosives including HMX and RDX, with unmodified SF-CO₂ as mobile phase. RDX appeared to give acceptable results, but HMX exhibited poor peak shapes and at least some irreproducibility, which were attributed to low solubility in SF-CO₂. No solubility, extraction, or other quantitative data, or use of cosolvent modifiers were actually described, although use of modifiers was suggested as a possibility. Griest, Guzman, and Dekker (1989) stated that such experiments were, however, "under way."

Matson et al. (1987) examined the solubility of solid rocket propellants and ingredients, including HMX and RDX, in SF-CO₂ and SF-NH₃. They used a flow-through extraction apparatus with UV detection to study the solubility of HMX in SF-CO₂; they found that HMX had essentially no ($<10^{-5}$ weight percent at 75° C and approximately 4,500 psi) solubility in SF-CO₂. RDX, whose molecular size is somewhat smaller than HMX, had measurable solubility and exhibited a nearly log-linear relationship with respect to CO₂ density. The effects on solubility of RDX in SF-CO₂ of the cosolvents dimethylsulfoxide (DMSO), dimethylformamide, and water were also examined in a static extraction apparatus; there seemed to be no noticeable increase due to presence of these cosolvents. However, when DMSO and N-methylpyrrolidine were studied with RDX and SF-CO₂ in the flow-through cell, the percent weight loss from the RDX sample per 100 g of SF-CO₂ increased from 1.4 to about 5. An attempt to extract RDX into reverse aqueous micelles suspended in a supercritical ethane medium was unsuccessful. However, using the same flow-through apparatus it was found that RDX was extensively soluble in supercritical ammonia.

Extraction of HMX and RDX in near-critical fluid ammonia or liquid ammonia has been described in reports by Kwak (1991) and Melvin (1992). It was found that HMX and RDX from rocket propellants could be solubilized, separated, and recovered by use of liquid NH₃; photographs of RDX and HMX recovered in this way are reproduced (Kwak 1991). This process is now being raised to the pilot plant scale (Reader et al. 1993). However, one potential problem seems worth mentioning. It was reported (Melvin 1992) that RDX underwent a mild degradation reaction over a 24-hour period in the presence of liquid ammonia; the nature and products of this decomposition were not described. HMX was found to be more stable, but may also exhibit the same decomposition reaction. Thus careful equipment design and material handling is required to minimize decomposition hazards of HMX and RDX, and especially nitroglycerine extracted from rocket propellants by this method. This is especially true in view of the report that nitro-containing explosives are sensitized by amines (Constantinou, Mukundan, and Chaudhri

1992); a similar effect might well take place during treatment of HMX/RDX with liquid ammonia. Additional concerns might be the odor and toxicity of ammonia.

3. STRUCTURE-SOLUBILITY RELATIONSHIPS

This section includes a review of available information on the relationship of molecular structure to solubility in SFs (with a few exceptions, most of this information pertains to SF-CO₂). This information provides a basis for the evaluation of the relationship between cosolvent-modifier properties and molecular structure, discussed in the following section.

3.1 Experimental Studies of Structure-Supercritical Solubility Relationships. Several of the early workers in SFE presented summaries or discussions of the effect of molecular structure on solubility in liquid CO₂ or in SF-CO₂. In general, they seem to agree with each other. These discussions are quoted or summarized in the following paragraphs. Then, the results of other studies will be summarized and compared with these relationships.

Francis (1954) amassed a great deal of very useful data on solubility of 261 organic compounds in liquid CO₂; strictly speaking, this data pertains to liquid rather than to SF-CO₂, but the temperatures and pressures seem high enough to make the data relevant to supercritical conditions also. Francis also made some comments on the relationship of structure to solubility:

"... The miscibilities of many other solvents with carbon dioxide may be predicted. Homologs differ only slightly in miscibility. With increasing molecular weight, solubilities may increase at first and then steadily decrease (e.g., aniline-toluidines-xylylene). Halogen atoms and carbonyl and ether groups also have slight effects (carbon tetrachloride, 2-octanol and *n*-butyl ether are all miscible with carbon dioxide); but hydroxyl, amino and nitro groups diminish solubility, especially if two or more are present. Complete mixing is prevented also by a bicyclic structure in derivatives (e.g., methoxynaphthalene) as well as in hydrocarbons. These effects are similar to but not quite parallel with those involved in hydrocarbon miscibilities."

Stahl et al. (1978), in the course of an article describing an apparatus for SFE-TLC, described some rules of thumb for extractability with CO₂:

- "(a) Hydrocarbons and other typically lipophilic organic compounds of relatively low polarity, e.g., esters, ethers, lactones, and epoxides, can be extracted in the lower pressure range, i.e., 70–100 bar.
- (b) The introduction of strongly polar functional groups (e.g., –OH, –COOH) makes the extraction more difficult. In the range of benzene derivatives, substances with three phenolic hydroxyls are still capable of extraction, as are compounds with one carboxyl and two hydroxyl groups. Substances in this range that cannot be extracted are those with one carboxyl and three or more hydroxyl groups.
- (c) More strongly polar substances, e.g., sugars and amino acids, cannot be extracted in the range up to 400 bar.
- (d) Fractionation occurs in the pressure gradient when there are greater differences in the commencement of boiling or sublimation, i.e., in the volatility, and/or marked differences in the polarity of the substances (DC value). The fractionation effects are most marked in the range where there is a sharp rise in the density and dielectric constant of fluid carbon dioxide."

Sims (1982), in the course of a no-reference discussion of use of SF-CO₂ for botanical extractions, presented some general conclusions about the solubilities of organic compounds in liquid (or SF?) CO₂, obtained from "pilot studies and other published material." These are quoted below:

- "Low-to-medium-molecular-weight oxygenated organic compounds such as esters, ketones, alcohols, ethers, and aldehydes are soluble (e.g., glycerol triacetate and camphor).
- Most low-molecular-weight nonpolar organic compounds including alkanes, alkenes, terpenes and other hydrocarbons are soluble (e.g., limonene and gasoline).
- Polar organic compounds such as carboxylic acids are soluble only if the molecular weight is very low (e.g., acetic acid).

- The presence of polar groups such as carboxyl, hydroxyl, or nitrogenous groups usually decreases the solubility of a compound.
- Chlorophyll, carotenoids, fruit acids, sugars, amino acids, and most inorganic salts are insoluble.
- Fatty acids and their glycerides have low solubility. However, esterification with mono-alcohol increases their solubility.
- Alkaloids are insoluble in liquid CO₂, but some are soluble in supercritical CO₂.
- Water solubility at 20° C is 0.1%."

Hyatt (1984) studied the solvent properties of liquid and SF-CO₂; a significant portion of his conclusions are based on liquid CO₂ rather than on SF-CO₂, but should be valid for SF-CO₂ since, as he points out, the differences between them are largely a matter of degree. He made the following observations with regard to solubility:

- "(1) Liquid CO₂ behaves like a hydrocarbon solvent, with a few notable points of difference (e.g., methanol miscibility).
- (2) Liquid CO₂ does not interact strongly with typical organic weak bases (e.g., anilines, pyrroles, pyridines), although it, of course, forms salts with aliphatic amines.
- (3) Liquid CO₂ has strong homogenizing action (i.e., many pairs of immiscibles or partially miscible liquids form a single phase when mixed with liquid CO₂).
- (4) Liquid CO₂ is a good solvent for aliphatic hydrocarbons up to at least the low C₂₀'s and for most small aromatic hydrocarbons. Few polycyclic hydrocarbons show appreciable solubility.

- (5) Halocarbons, aldehydes, esters, ketones, and low alcohols are freely soluble in CO₂. Higher alcohols (>C₁₀) are generally soluble enough for facile extraction. Glycols and glycerol have low solubility.
- (6) Phenols show poor solubility in CO₂, as do most anilines. Hydroquinones and other polycyclic aromatics are essentially insoluble.
- (7) Polar compounds, such as amides, ureas, urethanes, and azo dyes, exhibit poor solubility in CO₂.
- (8) Few materials of any structural type with molecular weights above around 500 are soluble in liquid CO₂."

The most complete and accessible discussion of solubility in liquid or SF-CO₂ is probably that of Dandge, Heller, and Wilson (1985), who obtained some additional data and discussed, in much more detail than did Francis, structure-solubility relationships for these systems and for those studied earlier by Francis (1954). They used the term "dense CO₂" to describe either liquid CO₂ or near-liquid SF-CO₂. The relationships described by Dandge, Heller, and Wilson (1985) are summarized here very briefly.

- Alkanes with less than 12 carbons are completely miscible with CO₂, but thereafter solubility decreases rapidly with increasing number of carbons. Branching leads to greater solubility, as does the presence of double bonds. On the other hand, aromatic compounds appear in general to be less soluble than their hydrogenated counterparts.
- Based on a very limited amount of data, halogenation on an aromatic ring has little effect on solubility but halogenation on an aliphatic side chain decreases it.
- Alcohols with six or less carbons are miscible with CO₂, but above six carbon atoms, solubility decreases sharply. Branching helps to increase solubility.
- Phenol has only 3% solubility in dense CO₂; etherification or addition of methyl substituents increases solubility, but other substituents may either increase or decrease solubility.

- Straight-chain carboxylic acids with less than ten carbons are completely miscible in dense CO₂, but solubility decreases very sharply thereafter. The presence of halogen, hydroxyl, or aromaticity decreases solubility.
- Etherification and esterification generally increase the solubility of alcohols, phenols, and carboxylic acids in dense CO₂.
- Low-molecular-weight aldehydes are generally miscible with dense CO₂, but addition of aromatic groups causes a great decrease in solubility.
- For amines, solubility generally decreases in the order tertiary>secondary>primary; N-alkyl substitution increases solubility, while addition of aromatic substituents decreases solubility. Basicity of amines has a tremendous effect on the solubility in dense CO₂, the more basic amines such as aliphatics tending to react with CO₂ to form carbonates. In the case of amides, N-alkyl substitution increases solubility, at least in the case of formamides and methyl or ethyl substituents.
- Nitro groups tend to decrease solubility, especially if more than one is present. The exact effect of chain length in nitroaliphatics has not been determined, although those homologs up to nitropropane are completely miscible in dense CO₂. Substituents have profound effects here, most leading to a decrease in solubility. (The low solubility of HMX and RDX in SF-CO₂, discussed above, is easily understandable in terms of this trend.)

Rizvi et al. (1986), in the course of a discussion of possible food-processing applications of SFE, summarized the solubility of organic compounds in SF-CO₂ as follows:

- "Materials with molecular weights above 500 Daltons have limited solubility.
- Low-to-medium molecular weight halocarbons, aldehydes, ketones, esters, alcohols, and ethers are very soluble.

- Low molecular weight, nonpolar aliphatic hydrocarbons with up to 20 carbons, and small aromatic hydrocarbons, are soluble.
- Polar Organics such as carboxylic acids are soluble if the molecular weight is very low. Amides, ureas, urethanes, and azo dyes exhibit poor solubility.
- Fatty acids and their triglycerides show low solubility; however, mono-esterification enhances fatty-acid solubility considerably.
- The addition of polar groups such as hydroxyl, carboxyl, or nitrogen generally decreases the solubility of the original compound.
- The solubility within a homologous series decreases with increasing molecular weight.
- Alkaloids, phenols, and most aniline compounds show poor solubility.
- Chlorophyll, carotenoids, amino acids, fruit acids, and most inorganic salts are insoluble."

Schmitt and Reid (1985) studied the solubility of naphthalene, 1,4-naphthoquinone and acridine in supercritical ethane, CO₂, fluoroform, and CF₃Cl. The solutes were chosen so that each contained a single substituent attached to a bi- or tricyclic aromatic system; the solvents were chosen for chemical disparity, yet nearly equal critical temperatures. They found that naphthalene was the most soluble, the substituents tending to reduce solubility. Among the solvents, the solutes were all least soluble in CF₃Cl, and the most noteworthy observation was probably that fluoroform (CHF₃), which was the next-to-worst solvent for naphthalene, became (over at least part of the range studied) the best solvent of the four for both naphthoquinone and acridine. This was attributed to hydrogen-bonding involving the proton in CHF₃, which is expected to be to some degree acidic.

Schmitt and Reid (1986b) also studied the solubility of some monofunctional aromatic compounds in SF-CO₂, ethane, chlorotrifluoromethane, and fluoroform; the emphasis was on the effect of solvent on solubility. It was found that ethane was a good solvent for aromatic hydrocarbons. Fluoroform was a poor solvent for hydrocarbons, but was a good solvent for molecules containing potential hydrogen-

bonding sites such as $>C=O$, $-NH_2$, and $-N=$ (since these groups are also polar, it seems uncertain to the present writer whether the improved solubility is due to polarity or to hydrogen-bonding). Carbon dioxide was a reasonably good general solvent for both polar and nonpolar compounds, while CF_3Cl was consistently the poorest of the four solvents studied.

Schmitt and Reid (1988) also studied the solubility of aliphatic hydrocarbons and their monofunctional derivatives in $SF-CO_2$. They found that solubility decreased with increasing chain length, and that addition of hydrogen-bonding substituents decreased solubility; other substituents were harder to classify in this regard. Phosphines were more soluble than their nitrogen analogs, although the role of vapor pressure was uncertain. In general, phosphines, ethers, thioethers, aldehydes, ketones, and nitriles were readily soluble in $SF-CO_2$, while alcohols, carboxylic acids, and tertiary amines were not. It was found that primary aliphatic amines had a tendency to react with $SF-CO_2$. Where comparison is possible, these trends are in general agreement with those summarized at the beginning of this section.

Kramer (1988) studied the solubility of several long chain (C_{14} - C_{16}) alcohols and carboxylic acids in $SF-CO_2$, and concluded that molecular weight and melting point were more important than chemical structure in determining the solubility of these substances.

The solubilities of a variety of substituted indole derivatives in SFs (CHF_3 , CO_2 , ethane, and ethylene) were studied by Sako et al. (1989), Sako, Kazunari, and Katayama (1988), and by Nakatani, Ohgaki, and Katayama (1989). It was found that for all compounds, SF-fluoroform was the best solvent of those studied. $SF-CO_2$ was the second best solvent for 5-aminoindole, oxindole, and 5-hydroxyindole but was the worst solvent for indole-3-aldehyde and indole-3-carboxylic acid. It was concluded that this variation was related to the fact that the first three compounds have π -electron donating substituents, while the last two have π -electron withdrawing substituents. In other words, compounds with electron-withdrawing substituents tend to have lower solubilities than those with electron-donating substituents.

Nakatani et al. (1991) studied the solubility of three pyrimidine derivatives (2-chloropyrimidine, 4-hydroxypyrimidine derivatives, and 2-mercaptopyrimidine) and two pyrazine derivatives (2-aminopyrazine and pyrazine-2-carboxylic acid) in $SF-CO_2$, SF-ethylene, SF-ethane, and $SF-CF_3H$. The compounds were generally more soluble in $SF-CO_2$ and $SF-CF_3H$ than in the hydrocarbon solvents. These data can be combined with those of Yamamoto, Ohgaki, and Katayama (1990), who found that unsubstituted pyrimidine was completely soluble in CO_2 and CF_3H . It was then concluded that for

for pyrimidines, solubility was decreased by all substituents, especially those that participate in hydrogen bonding.

Nakatani, Ohgaki, and Katayama (1991) studied the effect of substituents and solvents on the solubilities of naphthalene derivatives. They summarized their results in five rules for selection of solvents, which are summarized below. The first three rules concern dissolution power of solvents, while the last two concern substituent effects on solubility. The rules are as follows:

- (1) Hydrocarbons such as ethylene and ethane are good solvents for hydrocarbons because of the natural affinity between like compounds. However, introduction of polar functional groups into the solute causes a decrease in solubility in hydrocarbons.
- (2) Polar solvents such as trifluoromethane (CHF_3) are good solvents for all substances except for nonpolar hydrocarbons; the solubilities of polar but nonassociated compounds are especially high in these solvents.
- (3) SF-CO_2 is generally a fairly good solvent. An electron-releasing substituent makes it a better solvent, while electron-withdrawing substituents reduce its dissolving power.
- (4) Introduction of substituents generally tends to reduce solubility relative to the parent compound; the solubility of a disubstituted compound is additionally reduced relative to that of the monosubstituted compound.
- (5) Substituents that engage in hydrogen-bonding strongly lower solubility; but the presence of a second such substituent does not always lower the solubility relative to that of the monosubstituted compound.

These rules are generally in agreement with the preceding discussion.

In the course of a study of cosolvent effects (the main portion of this study is subsequently discussed in Section 4), Ekart et al. (1993) reported solvent effects for SF-CO_2 and for $\text{SF-CF}_3\text{H}$ relative to SF-ethane . These effects are included here as Table 2. It can be seen that hydrocarbons such as

Table 2. Solvent Effect for Supercritical CO₂ and Supercritical CF₃H Relative to Ethane, 50° C

| Solvent | CO ₂ | | | CF ₃ H | | |
|------------------------------------|-----------------|------|------|-------------------|------|------|
| Solute | Pressure (bar) | | | Pressure (bar) | | |
| | 120 | 150 | 200 | 120 | 150 | 200 |
| Fluorene | 0.28 | 0.42 | 0.5 | 0.39 | 0.39 | 0.37 |
| Dibenzofuran | 0.34 | 0.51 | 0.58 | — | — | — |
| Dibenzothiophene | 0.25 | 0.36 | 0.53 | 0.24 | 0.24 | 0.21 |
| Carbazole | 0.46 | 0.72 | 0.93 | 0.8 | 0.8 | 0.81 |
| Fluorenone | 0.44 | 0.71 | 0.87 | 1.23 | 1.37 | 1.53 |
| 9-Hydroxyfluorene | 0.55 | 0.93 | 1.13 | 0.73 | 0.8 | 0.84 |
| 2-Dimethylamino-9-Fluorenone (sic) | 0.39 | 0.68 | 0.80 | — | — | — |
| 2-Naphthol | 1.09 | 1.98 | 2.48 | 1.12 | 1.16 | 1.19 |
| Phenanthrene | 0.23 | 0.35 | 0.41 | — | — | — |
| Anthracene | 0.23 | 0.35 | 0.4 | 0.29 | 0.27 | 0.25 |
| 9-Cyanoanthracene | 0.34 | 0.58 | 0.74 | 0.82 | 0.85 | 0.85 |
| Acridine | 0.33 | 0.53 | 0.6 | 0.59 | 0.57 | 0.5 |
| Phenazine | 0.37 | 0.6 | 0.74 | — | — | — |
| Thianthrene | 0.2 | 0.32 | 0.38 | — | — | — |
| Hexamethylbenzene | 0.24 | 0.33 | 0.36 | — | — | — |

Source: Ekart et al. (1993).

fluorene, anthracene, and hexamethylbenzene are least soluble in SF-CO₂ relative to ethane, while more polar compounds such as fluorenone, 9-cyanoanthracene, 9-hydroxyfluorene, and 2-naphthol are more soluble in SF-CO₂ relative to ethane. The same trend continues in SF-CF₃H, although the more polar compounds are more soluble in SF-CF₃H than in SF-CO₂ relative to SF-ethane, as expected on the basis of the previous discussion. It is also interesting to note (Table 3) that the supercritical ethane-CHF₃ solvent effects vary much less with pressure than do the supercritical ethane-CO₂ solvent effects. The authors attribute this effect to the facts that (a) the change in solubility with pressure is faster when the pressure is closer to the critical point, and that (b) the critical point for ethane (48.8 bar) is closer to that for CF₃H (48.6 bar) than to that for CO₂ (73.8 bar).

Peters et al. (1989) studied the relationship between the number of carbons in straight-chain paraffins, and their solubility in supercritical solvents such as methane and CO₂. They found that the logarithm of the solubility decreased linearly with the number of carbons. This is also consistent with the trends found by Dandge and summarized at the beginning of this section.

Maheshwari et al. (1992) studied the solubility of fatty acids (lauric acid, C₁₁H₂₃COOH; myristic acid, C₁₃H₂₇COOH; palmitic acid, C₁₅H₃₁COOH; stearic acid [octadecanoic acid], C₁₇H₃₅COOH); oleic acid [9-octadecenoic acid]; and linoleic acid [9,12-octadecadienoic acid]) in SF-CO₂. Examination of their data indicates that, over most of the range of densities covered, an increase in the number of carbon atoms led to a decrease in solubility; this is in agreement with the preceding discussion. Plots of solubility vs. density showed too much curve-crossing to allow a conclusion with regard to the effect of unsaturation on solubility of these compounds in SF-CO₂.

3.2 Theoretical Studies Relevant to Structure-Supercritical Solubility Relationships. For the sake of brevity, only those theoretical studies most relevant to structure-supercritical solubility relationships, and to the prediction of supercritical solubility from molecular structure will be considered in this section.

One approach has been to calculate the solubility from quantities which can in some way be calculated directly from the molecular structure of the solute. For example, Gangadhara Rao and Mukhopadhyay (1990) calculated supercritical solubilities of solids in supercritical CO₂, ethane, and ethylene by using a covolume-dependent mixing rule with the Peng-Robinson equation of state. The compounds considered included several polycyclic aromatic hydrocarbons and substituted benzenes and naphthalenes, as well as skatole and 5-methoxyindole.

Table 3. Normalized Cosolvent Effects in Supercritical Ethane (3% Cosolvent, 150 bar, 50° C)

| Solute | Ethanol | Isopropanol | Acetone | CHCl ₃ | 111-TCE | 222-TFE | TEA | 12-DBE |
|-------------------------|---------|-------------|---------|-------------------|---------|---------|------|--------|
| Fluorene | 0.99 | 1.00 | 1.17 | 1.20 | 1.18 | 1.16 | 1.21 | 0.88 |
| Dibenzofuran | 0.97 | 1.00 | 1.14 | 1.15 | 1.16 | 1.12 | 1.31 | 0.87 |
| Dibenzothiophene | 0.98 | 1.02 | 1.13 | 1.24 | 1.29 | 1.16 | 1.38 | 0.88 |
| Carbazole | 1.91 | 1.72 | 1.76 | 1.42 | 1.38 | 2.14 | 1.60 | 1.01 |
| Fluorenone | 1.07 | 1.10 | 1.21 | 1.39 | 1.19 | 2.64 | 1.48 | 0.87 |
| 9-Hydroxyfluorene | 2.05 | 1.90 | 1.36 | 1.24 | 1.19 | 3.46 | 2.28 | 0.89 |
| 2-Dimethylaminofluorene | 1.29 | 1.25 | 1.35 | 1.63 | 1.37 | 4.28 | 1.80 | 1.01 |
| 2-Naphthol | 4.59 | 3.82 | 2.90 | 1.91 | 1.72 | 5.06 | 3.16 | 1.41 |
| Phenanthrene | 0.98 | 1.01 | 1.14 | 1.20 | 1.19 | 1.17 | 1.35 | 0.91 |
| Anthracene | 0.97 | 1.02 | 1.12 | 1.27 | 1.19 | 1.14 | 1.39 | 0.86 |
| 9-Cyanoanthracene | 1.08 | 1.08 | 1.25 | 1.34 | 1.23 | 2.46 | 1.67 | 0.88 |
| 2-Aminoanthracene | 1.39 | 1.25 | 1.37 | 1.45 | 1.22 | 2.07 | — | 0.87 |
| Acridine | 1.26 | 1.20 | 1.27 | 1.58 | 1.19 | 4.56 | 1.70 | 0.91 |
| Phenazine | 1.11 | 1.11 | 1.22 | 1.43 | 1.19 | 3.39 | 1.43 | 0.88 |
| Thianthrene | 0.99 | 1.02 | 1.16 | 1.26 | 1.24 | 1.20 | 1.46 | 0.90 |
| Hexamethylbenzene | 1.02 | 0.98 | 1.13 | — | — | 1.33 | — | — |
| Cholesterol | 1.90 | 1.79 | 1.43 | — | — | 4.08 | — | — |

Source: Ekart et al. (1993).

Very briefly, the solubility of a solid in an SF can be expressed as

$$y_i = (P_i^{\text{sat}} \exp[v_i^s(P - P_i^{\text{sat}})/RT]) / (\phi_i P) \quad (1)$$

where $i = 1$ and 2 signify the solvent and solid components, respectively. The mole fraction of solid in the SF phase is defined as y , while T , P , and R are the equilibrium pressure, temperature, and the universal gas constant, respectively. The saturation vapor pressure and the molar volume of the solid are, respectively, represented by P^{sat} and by v^s . The fugacity coefficient of the solid is represented by ϕ_i and is calculated from the Peng-Robinson equation of state. The mathematical equation from which ϕ_i is calculated involves, in addition to y_i , temperature, pressure, and quantities dependent on the solvent (and available in the literature, at least for SF-CO₂, ethane, and ethylene (Gangadhara Rao and Mukhopadhyay 1990)), only the van der Waals volume of the solute and its heat of vaporization.

Now, Bondi (1968) has shown that, for many common molecules, these quantities can be calculated by summing group contributions for each group or component of the solute molecule. It, therefore, follows that the solubility of a solid solute in a SF can be estimated, given only the structure of the solid and which SF is of interest. Solubilities estimated in this way gave an average deviation of 22% from experimental values; the authors considered this encouraging but pointed out the need for further work. For further details of the calculations, the reader is referred to Gangadhara Rao and Mukhopadhyay (1990).

Later, Mukhopadhyay and Raghuram Rao (1993) calculated the solubility of solutes in modified and unmodified SF-CO₂ using a modified version of the covolume-dependent (CVD) mixing rule. Their goal was to predict the solubility of mixed solutes from minimum information, such as the pure component solubilities. The model was able to predict the solubility data at various temperatures. To make the model more predictive, the CVD interaction parameter was correlated with pure-component properties, such as molar volume, van der Waals volumes, and dipole moments. However, this approach did not give an adequate representation of the stronger solute-cosolvent interactions; further work is therefore needed on prediction of cosolvent effects.

A related approach was followed by King and Friedrich (1990), who used a reduced solubility parameter approach to estimate supercritical solubility. The reduced solubility parameter is defined by the equation

$$\Delta = \delta_1/\delta_2, \quad (2)$$

where Δ is the reduced solubility parameter, δ_1 is the solubility parameter of the solvent supercritical gas defined by

$$\delta_1 = 1.25P_c^{1/2}(\rho_{r,SF})/(\rho_{r,liquid}), \quad (3)$$

and δ_2 is the solubility parameter of the solute, which is represented by

$$\delta_2 = (\Sigma\Delta\epsilon_i/\Sigma v_i)^{1/2}, \quad (4)$$

where P_c is the fluid critical pressure, $\rho_{r,SF}$ is the reduced density of the critical fluid, $\rho_{r,liquid}$ is the reduced density of the fluid in the liquid state, $\Sigma\Delta\epsilon_i$ is the energy of vaporization (calculated as the sum of group contributions, one for each of the substituent groups in the solute molecule), and Σv_i is the molar volume of the solute (also calculated as a sum of group contributions). For further details of the calculations, the reader is referred to King and Friedrich (1990).

The use of this method is exemplified by caffeine. Its solubility parameter was calculated using the group contributions of Fedors (1974); a value of 12.96 was obtained, leading to a reduced solubility parameter of 0.44. Together with a plot of reduced solubility parameter against solubility given by King and Friedrich (1990), this value gave a weight fraction solubility of 4.0×10^{-4} for caffeine in SF-CO₂ under the conditions of the plot. This was in reasonable agreement with the experimental value (Schilz 1978) of 3.3×10^{-4} .

Reduced solubility parameters calculated as described earlier were plotted against approximate distribution coefficients calculated from the data in the literature; it was found that, at least for similar types of compounds, reasonable correlations between reduced solubility parameter and solubilities or distribution coefficients could be obtained.

Solubility parameter values for solutes were used together with Hansch-Leo log P values (a measure of hydrophobic interactions) for the same solutes by Kane et al. (1993). Like solubility parameters, log P values can be estimated by a system of group additivities. What was novel about this work was the use of hydrophobicity as an aid to solubility prediction; the use of solubility parameters for this purpose was

described in the preceding paragraphs. For a series of fluoro- and hydroxybenzophenones, it was found that log P values and solubility parameters both gave satisfactory correlations with solubilities (mole fraction) in SF-CO₂.

Another approach to the estimation of supercritical solubilities involves correlation of solubility with micromolecular properties calculated by quantum-mechanical methods.

Politzer et al. (1992) carried out molecular orbital calculations, at the ab initio Hartree-Fock STO-5G//STO-3G level, on the nine naphthalene and indole derivatives studied earlier (Sako, Kazunari, and Katayama 1988; Sako et al. 1989; Nakatani, Ohgaki, and Katayama 1989). Good correlations were found between solubility in four SFs (CO₂, ethane, ethylene, and CHF₃) and the sum of the variances between positive and negative potentials on the solute molecular surfaces (σ_{tot}^2). The solubility decreased as the total variance increased. In other words, solubility appears to decrease with increasing polarity, in agreement with the tendencies discussed in the preceding section.

This conclusion was later extended (Politzer et al. 1993a) to an additional 21 organic compounds, including substituted benzenes, naphthalenes, and indoles. Solubility in these systems seemed to be favored by a relatively slowly varying surface potential and to be impeded by sudden changes and strong extrema. This is in agreement with the tendencies found and discussed in the preceding section. In addition, it was found that the solubility decreased with increasing molecular volume.

Politzer et al. (1993b) calculated several molecular properties related to size and interaction tendency for a group of three toxic molecules. Two of these properties, the molecular volume and σ_{tot}^2 , were used to quantitatively predict supercritical solubility using equations of the form

$$\ln (\text{solubility}) = \alpha(\text{vol})^{-1.5} - \beta(\sigma_{\text{tot}}^2)^2 - \gamma,$$

where vol is the molecular volume, σ_{tot}^2 is defined above, and α , β , and γ are positive constants dependent on the pressure and temperature. The same calculations were also carried out on five proposed simulants for these molecules, and it was proposed that 1,5-dichloropentane was a promising simulant for sulfur mustard, with regard to supercritical solubility and supercritical water oxidation.

Although solubility in SF solvents was not explicitly considered, it may be of interest to the reader that Murray et al. (1993) have demonstrated a relationship between computed molecular surface properties such as those described earlier, to critical properties such as critical temperature and critical pressure, and to boiling points.

Even more elaborate equations were used by Famini and Wilson (1993), who adapted the linear solvation energy relationship (LSER) (Kamlet et al. 1983) to the estimation of supercritical solubilities with the help of molecular orbital theory. They refer to this approach as the theoretical linear solvation energy relationship (TLSER). The general form of the LSER is given by

$$\log(\text{property}) = \text{bulk/cavity term} + \text{polarizability/dipolarity term} + \text{hydrogen bonding term}$$

where "property" denotes the property under consideration (in the present case, solubility in SF-CO₂ or other SF solvent). The bulk/cavity term represents the work done displacing the solvent and making a hole for the solute molecule; it is considered to be proportional to the molecular van der Waals volume (V_{mc}), given in Å³. The dipolarity/polarizability term is a measure of the ability of an electron cloud to be polarized by an electric field; it is considered to be proportional to the polarizability index (π_i); this is a dimensionless quantity obtained by dividing the polarization volume by the molecular volume. The hydrogen-bonding term is divided into two terms in the LSER, one representing hydrogen-bonding involving a solute proton (HBA term) and one representing hydrogen-bonding involving a solvent proton (HBB term). In the TLSER, these effects are further subdivided into covalent and electrostatic terms. The covalent HBB contribution is considered proportional to the molecular orbital basicity (ϵ_B); it is computed by subtracting the energy of the highest occupied MO (HOMO) of the solute from the energy of the lowest unoccupied MO (LUMO) of water. The covalent HBA contribution is the molecular orbital acidity; it is computed analogously by subtracting the HOMO of water from the LUMO of the solute. The electrostatic basicity, q^- , is considered to be the magnitude of the most negative formal charge in the molecule. The electrostatic acidity, q^+ , is the charge of the most positive hydrogen atom in the molecule. The above terms are calculated using the MNDO molecular orbital method, as contained within MOPAC v6.0; further details are given by Famini and Wilson (1993).

The general form for the TLSER equation is then given by

$$\log P = P_0 + aV_{mc} + b\pi_i + c\epsilon_B + dq^- + e\epsilon_\alpha + fq^+,$$

where a, b, c, d, e, and f are proportionality constants. The following TLSE equation then relates the solubility (apparently in water) of the 22 solutes considered, to their solubility in SF-CO₂ at 14 MPa and 308 K:

$$\log S_{\text{CO}_2}^{14 \text{ MPa}} = -6.037\pi_i + 10.440\epsilon_\beta - 22.098q^- + 24.350q^+ - 8.370,$$

where S is solubility in mole fraction. A similar equation was obtained for solubility in SF-CO₂ at 20 MPa. Solubilities of several toxic molecules and simulants were calculated and the results compared with those obtained by Politzer et al. (1993b); agreement was found to be fairly good. It was also pointed out that examination of the correlations can yield insight into the factors affecting solubility.

The above work is also described briefly by Cramer, Famini, and Lowrey (1993); this reference also includes considerable background on the types of correlation and calculations involved.

Battersby et al. (1993) used computational chemistry and neural network software to calculate heat of formation for an assembly of a naphthalene molecule surrounded by 120 CO₂ molecules; from such numbers it should be possible to calculate heats of solution and hence obtain some estimate of relative solubilities.

Although the results to date give cause for optimism, further work is clearly needed on both of the above approaches to theoretical estimation of supercritical solubility.

4. STRUCTURE-MODIFIER PROPERTY RELATIONSHIPS

The solubility of solid organic solutes in SFs can often be enhanced by the addition to the supercritical solvent of a small amount (1–10%) of an additive. This additive is known as a "cosolvent modifier" or "entrainer." The solubility-enhancement effect can be quite dramatic, sometimes amounting to several orders of magnitude. This effect can be quite useful in laboratory or process applications involving SFE or SFC. If the solubility of one component of a mixture is enhanced more than that of another, it is sometimes possible to improve the selectivity of an extraction.

In this section, the effect of the chemical structure of a cosolvent modifier on its ability to enhance solubility in a SF will be reviewed. The emphasis will be on SF-CO₂, although it will also become

necessary to discuss other solvents. The emphasis will be on SFE, although results from SFC will be discussed as appropriate. It should be remembered, however, that in the case of SFC, the cosolvent may have an effect on the stationary phase as well as on the mobile phase; for example, it may occupy or cover up active sites on the stationary phase.

We will begin by reviewing a recent paper (Ekart et al. 1993) that gives considerable information on cosolvent effects for 17 solutes and 8 cosolvents in the solvents SF-ethane, SF-CO₂, and SF-fluoroform. Solubilities were measured by a chromatographic method, in which the solubility of a solute in a solvent-cosolvent mixture was determined from SFC retention time on a column; the column was the same for all measurements made.

These authors define a cosolvent effect by the equation

$$\Psi = (y_i^{\text{sat}''})/(y_i^{\text{sat}'}), \quad (5)$$

where Ψ is the cosolvent effect, $y_i^{\text{sat}''}$ is the solubility of solute i in the modified solvent and $y_i^{\text{sat}'}$ is its solubility in the unmodified solvent. To compare data better, they attempted to remove the portion of the cosolvent effect Ψ that is due to the density increase that occurs on addition of cosolvent; this density increase was estimated from the solubility isotherms in pure ethane. Quantitative comparison was facilitated by calculating Ψ for 3 mole percent cosolvent, assuming that Ψ was related linearly to the mole fraction of cosolvent. Due to the approximations introduced in removing the density and composition dependence of Ψ , there may be some uncertainty in comparing Ψ for a solute across different cosolvents, but there should be no problem looking at several solutes in the same cosolvent mixture.

Table 3 shows cosolvent effects for SF-ethane taken from Ekart et al. (1993, Table 5). Uncertainties in these cosolvent effects were estimated to be 10–15% at most, with most of this occurring at lower pressures, nearer the critical point. Ekart et al. also includes tables of solvent effects for SF-CO₂ relative to SF-ethane and for SF-fluoroform relative to SF-ethane; but these refer to solvent effects on solubility of solutes, not to solvent effects on cosolvent effects. The data from Ekart et al. tables is included as Table 2 in the present report, and is discussed in Section 3.1.

It is true that these cosolvent effects (Table 3) are given for SF-ethane, not for SF-CO₂; however, the cosolvents should interact with the solutes in a generally similar way in SF-ethane, in SF-CO₂, and in

SF-fluoroform. Therefore, it might be worthwhile to compare the cosolvent effects for the various cosolvents and solutes; this comparison suggests that for a strong cosolvent effect to be observed, there must be a specific interaction of some sort between the cosolvent and the solute.

To begin, compare (Table 3) the solutes fluorene and fluorenone; these are similarly shaped molecules which differ mainly in that fluorenone can act as a hydrogen-bond acceptor and also as an electron acceptor in charge-transfer interactions. For the cosolvents acetone, 1,1,1-trichloroethane (abbreviated 111-TCE in the table) and 1,2-dibromoethane (12-DBE), which have no particular specific interaction with the solutes, the cosolvent effects are near unity, i.e., no noticeable effect is observed. For the hydrogen-bond-donor cosolvents ethanol, isopropanol, and chloroform, differences in cosolvent effects between fluorene and fluorenone are noticeable but not large. For the strong hydrogen-bond donor, 2,2,2-trifluoroethanol (222-TFE), the cosolvent effect is much larger for fluorenone, as expected on the basis of fluorenone's ability to act as a hydrogen-bond acceptor. There is also a noticeable cosolvent effect on fluorenone relative to fluorene when triethylamine (TEA) is used as cosolvent; this is explainable on the basis of charge-transfer complexation between the electron pair in TEA and the electron-deficient pi-electron system in fluorenone.

Another illustrative example is provided by anthracene, 9-cyanoanthracene, and 2-aminoanthracene. The major effect here (Table 3) occurs in the case of the strong hydrogen-bond donor cosolvent, 222-TFE, which has little if any cosolvent effect on anthracene but has quite a strong effect on 9-cyanoanthracene and on 2-aminoanthracene; this is expected on the basis of the ability of these last two compounds to act as hydrogen-bond acceptors. TEA also has a significant effect in the case of 9-cyanoanthracene; this is expected on the basis of charge transfer complex formation between TEA and the electron-deficient pi-electron system in 9-cyanoanthracene. The hydrogen-bond acceptor 2-aminoanthracene also shows some tendency to associate with the hydrogen-bond donors ethanol, isopropanol, and chloroform. Significant cosolvent effects of acetone with solutes 2-aminoanthracene and 9-cyanoanthracene are explained (Ekart et al. 1993) in terms of an addition complex between the carbonyl group of acetone and the amino group of 2-aminoanthracene and a dipole-dipole interaction, respectively.

Another interesting compound is 2-naphthol, which displays the largest cosolvent effects of any solute studied. Most of these are explainable in terms of its tendency to function as both a hydrogen-bond donor and acceptor. However, 2-naphthol also exhibits noticeable solubility-enhancement effects in the presence of the cosolvents 111-TCE and 12-DBE, which are not capable of forming strong hydrogen bonds. These

effects, and similar ones for carbazole and 2-dimethylaminofluorenone, are explained by Ekart et al. (1993) in terms of enhancement of the polarity and polarizability of the fluid on addition of cosolvents 111-TCE and 12-DBE.

In similar ways, Ekart et al. (1993) explain all of the cosolvent effects demonstrated in Table 3 in terms of specific interactions. In general, it appears that strong cosolvent effects are observed only in cases where there are strong, specific interactions such as hydrogen bonding or charge-transfer interactions, although smaller effects, exemplified (preceding paragraph) by 111-TCE and 12-DBE and explainable in terms of polarity or polarizability enhancement, are sometimes observed.

It should be remembered that the results discussed above were obtained for SF-ethane, and strictly speaking are valid only in that solvent. However, it seems reasonable to suppose that the general conclusions and trends should also be valid for the cases of SF-CO₂ and SF-CF₃H. This is consistent with the report (Politzer 1992, Table 1) that the solubilities of a series of compounds (including naphthalene and a number of indole derivatives capable of hydrogen bonding) showed similar trends in the solvents SF-ethane, SF-ethylene, SF-CO₂, and SF-CF₃H. One possible cause for concern here might arise from the presence, on the oxygen atoms of the CO₂ molecule, of lone pairs of oxygen electrons which might be capable of acting as hydrogen-bond acceptors, thereby competing with solutes and tending to reduce the hydrogen-bonding effects in the data of Ekart et al. (1993) (preceding paragraphs). However, in view of the similarity of solvent effects on solubility, it does not seem unreasonable to suspect that hydrogen bonding of solutes to SF-CO₂ will not have an overwhelming effect on trends in cosolvent effects.

Brunner and Peter (1982) studied cosolvent effects on the solubilities of fatty acid glycerides and of palm oil (a mixture of fatty acid glycerides). Comparison of their Figures 4 and 8 shows that at 70° C and 200 bar, 10% ethanol increased the solubility of palm oil in SF-CO₂ from ca. 0.3 weight-percent to ca. 6 weight-percent, a factor of about 20. Acetone, benzene, hexane, formaldehyde diethylacetal, CH₂Cl₂, and CHCl₃ were tried out as cosolvent; these apparently caused no appreciable solubility increase, since it was concluded that "most substances do not enhance the distribution power in a certain system."

Blilie and Greibrokk (1985) studied the effect of various organic cosolvents on the SFC retention of a series of polycyclic aromatic hydrocarbons, nitrated polycyclic hydrocarbons, polystyrenes, and more polar compounds on reversed-phase C₁₈ columns. They found that 1-alkanols reduced retention more than branched alcohols, and that increasing chain length increased the cosolvent effect up to 1-hexanol. Higher

alcohols gave about the same retention as 1-hexanol. Straight-chain alcohols decreased retention more than did branched alcohols. Hexane and methyl-t-butyl ether had little effect, while acetonitrile and the cyclic ethers, dioxane and tetrahydrofuran, resulted in significant reductions in retention. The modifiers were considered to reduce retention both by deactivating the stationary phase and by modifying the eluting power of the solvent. The former explanation was favored since straight chain alcohols decreased retention more than branched ones, which was interpreted as the result of easier access to active sites. Nevertheless, it is possible that use of higher alcohols as cosolvents might lead to improved extraction efficiency for polar compounds capable of acting as hydrogen-bond acceptors, such as HMX and RDX, in supercritical CO₂.

Wong and Johnston (1986) studied the effects of cosolvents (methanol, ethanol, acetone) on the solubilities of cholesterol and stigmasterol. However, as pointed out by these authors, stigmasterol forms complexes with ethanol and methanol, and cholesterol form complexes with ethanol. Therefore, for the purposes of the present review, it is difficult to say more than that all three cosolvents appear to increase the solubility of these solutes by factors of 1.6 to ca. 10; any structure-modifier relationships proposed would be of dubious value due to the complex formation.

Tavana et al. (1989) attempted to develop a systematic method for selecting cosolvents for SF solubilization of organic compounds; in the course of this they examined the cosolvent effects of dichloromethane, butyl acetate, cyclohexanone, ethanol, methanol, and acetone on the solutes griseofulvin, digoxin, cholesterol, stigmasterol, and 2-aminobenzoic acid. However, because of the tendency of all of these solutes, except 2-aminobenzoic acid, to react or to form complexes with the cosolvents, it is hard to say more than that all of the cosolvents except dichloromethane (which had little if any effect) raised solubility of one or more of the solutes by factors between 1 and 10.

Roop and Akgerman (1989) studied the use of entrainers for supercritical extraction of phenol from aqueous solutions. They carried out calculations of the distribution coefficient, using the Peng-Robinson equation of state with a modified mixing rule, for a variety of hydrocarbon entrainers including simple alkanes, chloromethanes, and substituted benzenes. The best entrainers were the substituted benzenes, followed by the single alkene (1-pentene) used; simple alkanes were calculated to be the least efficient entrainers. They then studied the most promising entrainers, benzene and chlorobenzene, in an extraction bomb; methanol was also studied. Benzene was found to be the entrainer of choice. Methanol was found to have little or no effect on the distribution coefficient. In this case, the inefficiency of methanol as an

entrainer is understandable in view of its infinite solubility in, and tendency to form hydrogen bonds to, water.

Moriyoshi (1989) studied the modification of $\text{SF-N}_2\text{O}$ by cosolvents such as hexane, 1,2-dichloroethane, ethanol and water; solutes studied included naphthalene, anthracene, phenanthrene, pyrene, benzoic acid, and salicylic acid. The results were discussed in terms of specific interactions and changes in dielectric constant. However, the original paper is in Japanese and a translation is not yet available.

Ikushima, Goto, and Arai (1987) studied the effect of some cosolvents on solubilities of some hydrophobic biomolecules such as triolein, tristearin, lipids, and dl- α -tocopherol. The cosolvents studied were hexane, ethyl acetate, methylene chloride, acetone, ethanol, and diethyl ether. It was found that the first three entrainers enhanced solubility of these solutes by between 1 and 4, while the last three entrainers decreased it. These results were correlated with molecular cohesive energies and with modified solubility parameters. For the large hydrophobic molecules studied here, it perhaps not surprising that ethanol was not a good cosolvent.

Schmitt and Reid (1986a) studied the solubilities of phenanthrene and benzoic acid in SF-CO_2 and in SF-ethane , using benzene, acetone, methylene chloride and cyclohexane as cosolvents. They used an apparatus in which the solvent-entrainer mixture was passed through extraction columns packed with the solute of interest. It was found that the solubilities of both solutes increased with increasing entrainer concentration, but that it made little difference which entrainer was used; the greatest enhancement was that in the solubility of benzoic acid using acetone as modifier in SF-ethane . This is as expected on the basis of the expected ability of the acidic proton of benzoic acid to hydrogen bond to the unshared electrons on the oxygen atom of acetone. Comparison with two elementary theoretical models suggested that the data were better understood by considering the entrainer (or cosolvent) to be a second solvent in a solvent mixture rather than as a modifier of the SF density. A similar conclusion was reached with regard to solubilities of naphthalene and benzoic acid in an SF gas mixture containing 6.2% ethane in SF-CO_2 ; these solubilities also fell at values intermediate between the solubilities of the solutes in the pure supercritical solvents, suggesting again that the entrainer effected chemical modification of the solvent power of the fluid rather than just modifying the solvent's P-V-T properties.

Van Alsten (1986), and apparently Van Alsten, Hansen, and Eckert (1984), used an extraction-column apparatus to study the effect of the cosolvents methanol and acetone on the solubilities in SF-CO₂ of a number of organic solutes. The solutes used were from three different chemical classes: (1) a number of hydrocarbons such as anthracene, phenanthrene, and fluorene; as well as (2) the relatively nonpolar heteroatomic compound dibenzofuran; and (3) acridine (9-aza-anthracene), phenazine (9,10-diaza-anthracene), and fluorenone. It was found that methanol was a considerably better cosolvent than acetone (which was also a good cosolvent) for the aza-anthracenes acridine and phenazine, while acetone and methanol were both good cosolvents for fluorenone, with acetone being slightly better. Small cosolvent effects were noted for the remaining solutes. These results were attributed to (a) hydrogen-bonding between methanol and the pyridine-type nitrogen atoms in acridine and phenazine; to (b) dipole-dipole coupling of acetone with fluorenone and with the more polar monoaza-anthracene acridine; and to (c) causes of uncertain nature.

Walsh, Ikonomou, and Donohue (1987) used the data, summarized in the preceding two paragraphs (Schmitt and Reid 1986a; Van Alsten, Hansen, and Eckert 1984) in an attempt to understand the cosolvent effect. They explained the findings of Van Alsten, Hansen, and Eckert (the solute whose solubility in SF-CO₂ was most enhanced by methanol was acridine, with fluorenone as a distant second) and of Schmitt and Reid (significant cosolvent effect for solute benzoic acid in SF-ethane, with acetone as cosolvent, but not for any other system studied) by proposing that a significant specific interaction between cosolvent and solute is necessary for a large cosolvent effect to be observed. In the above cases, that effect is formation of a hydrogen bond either (a) between the OH of benzoic acid and the ketone oxygen of acetone, or (b) between the hydroxyl hydrogen of methanol and the pyridine-type nitrogen atom of acridine; these were discussed in terms of the hydrogen-bonding solvatochromic parameters α and β (Kamlet et al. 1983). However, Walsh, Ikonomou, and Donohue (1987) also discuss the possibility that formation of charge-transfer complexes could also cause significant solubility enhancement.

They also studied the infrared absorption of the systems studied by Van Alsten, Hansen, and Eckert (1984), using acetone as solvent because its oxygen was considered a good model for the oxygens of CO₂. It was found that only the acridine-methanol system gave evidence of complex formation. A similar experiment on the compounds studied by Schmitt and Reid (1986a), using hexane as solvent and benzoic acid as solute, resulted in a finding that a complex was formed only with the cosolvent acetone.

These results are in agreement with the above results of Ekart et al. (1993) in that they suggest that, in order for a large cosolvent effect to be observed, it is necessary for a significant specific interaction between the cosolvent and solute molecules. This interaction might take the form of, for example, a hydrogen-bonding or a charge-transfer interaction; a dipole-dipole interaction might also be a source of a cosolvent effect.

Dobbs et al. (1987) studied cosolvent effects in SF-CO₂ using a flow apparatus. Solutes included benzoic acid, 2-aminobenzoic acid, acridine, 2-naphthol, hexamethylbenzene and phthalic anhydride. Cosolvents included acetone, methanol, n-pentane and n-octane. It was found that all of the solvent-cosolvent combinations led to some solubility enhancement. However, the strongest effects, up to a factor of 6, are observed when a hydrogen bonding interaction is possible between the solute and cosolvent, for example between benzoic acid and methanol. The results were correlated by the use of a modified Van der Waals equation of state, and could be predicted qualitatively by calculating the attraction constants using dispersion, orientation, acidic and basic solubility parameters. A later paper (Dobbs and Johnston 1987) applied these results to these separation of mixtures.

Dobbs, Wong, and Johnston (1986) used a flow apparatus to study the use of aliphatic hydrocarbons to enhance the solubility of phenanthrene and hexamethylbenzene in SF-CO₂. They found that pentane, octane, and undecane increased the solubility by factors ranging from 1.5 to 5.4 at 35° C, depending on cosolvent concentration and on the chain length of the cosolvent. The cosolvent effect increased with increasing chain length of the modifier.

Schaeffer, Zalkow, and Teja (1988) studied the solubility of the drug precursor monocrotaline in SF-CO₂; it was found that ethanol had a cosolvent effect of 25-fold in the range of 308.15–328.15 K and 8.86–27.41 Mpa.

It has been reported (Johnston, McFann, Peck, and Lemert 1989) that tri-n-butylphosphate has a strong (factor of 300) cosolvent effect on the solubility of hydroquinone in SF-CO₂; this was attributed to an acid-base interaction, not a general dipolarity effect.

Cygnarowicz, Maxwell, and Seider (1990) used a commercially available SFE extractor to study the effect of the cosolvents methanol, ethanol, and CH₂Cl₂ on the solubility of the hydrocarbon β -carotene in SF-CO₂. The indicated cosolvents all increased the solubility, with the largest increase occurring in

the case of ethanol. The hydrogen-bonding interpretation of alcohol cosolvent effects seems uncertain here because of the hydrocarbon nature of the solute; however, it is not impossible that the OH protons of the alcohols could hydrogen-bond to the extended π -electron system of β -carotene.

Liu et al. (1990) studied the use of the cosolvents methanol, toluene, and dimethyl sulfoxide (DMSO) in the extraction of chlorinated aromatics from soil samples with SF-CO₂. They found that methanol was the strongest cosolvent, with DMSO being almost as good. Toluene usually had some effect, but was not as good as the other compounds studied. These results are consistent with the hydrogen-bonding properties of the compounds in question; methanol and the chlorophenols are capable of acting as both hydrogen-bond donors and acceptors, while the oxygens on DMSO should be capable of acting as hydrogen-bond acceptors. Toluene has little hydrogen-bonding capability.

Ting et al. (1993a) studied the effect on the solubility of naproxen ((S)-6-methoxy- α -methyl-2-naphthaleneacetic acid) in SF-CO₂ of six cosolvents. A flow technique coupled with gravimetric analysis was used. It was found that the solubility enhancement was considerable, and increased in the order ethyl acetate, acetone, methanol, ethanol, 2-propanol, and 1-propanol. The solubility increase was nonlinear with cosolvent concentration. Use of the Peng-Robinson or the Soave-Redlich-Kwong equations of state to correlate the results required negative binary interaction parameters, indicating strong interactions between naproxen and the cosolvents. It was concluded that the cosolvent effects were not explainable by any single property but were influenced both by hydrogen bonding and by relative distance from the CO₂-cosolvent binary critical point.

Ting et al. (1993b) used a model proposed by Ekart and Eckert to study these results; this model incorporated chemical equilibria into the Soave-Redlich-Kwong equation of state. The model worked well, and the equilibrium constants obtained could be correlated, by a linear free energy relationship, with the Kamlet-Taft solvatochromic parameters α , β , and π^* . It was stated that this correlation suggests that both chemical and physical factors are important in the interactions of these systems with naproxin.

Note that the cosolvent effects of the alcohols were reported to increase in the order of methanol, ethanol, and propanol; this is consistent with the findings of Blilie and Greibrokk (1985) that the cosolvent effects of alcohols in SFC increase with increasing chain length of the alcohol, up to hexanol.

Gurdial et al. (1993) studied the effect of cosolvents on the solubility of *o*- and *m*-hydroxybenzoic acids in SF-CO₂ in the range of 318–328 K and 90–200 bar. Measurements were made with a continuous-flow saturation apparatus. They found that addition of methanol or acetone caused solubility increases of up to an order of magnitude, with the larger increases being caused by methanol. By plotting solubility against density, it was found that these increases in solubility cannot be explained by changes in density. Since methanol can hydrogen-bond to the solutes much more efficiently than acetone, these results are consistent with the idea that a cosolvent capable of a hydrogen-bonding interaction with the solute will be a more efficient cosolvent.

Foster et al. (1993) studied the solubility of cholesterol in SF-ethane and in SF-CO₂, with the cosolvents hexane and acetone, as a function of density, temperature, pressure, and cosolvent concentration. They found an unusual reversal of cosolvent effects between the primary SFs, ethane and CO₂. In SF-ethane, acetone was a better cosolvent than hexane, but in SF-CO₂, hexane was the better of the two cosolvents studied. This was interpreted in terms of variations in dipole-dipole, dipole-quadrupole, and hydrogen-bonding effects between solvent SF-CO₂, the hydroxyl group of cholesterol, and the carbonyl group of acetone on the one hand, and solvent-solute dispersion forces involving the hydrocarbon portion of the cholesterol molecule on the other.

5. SOLVATOCHROMIC PARAMETERS FOR MODIFIED AND UNMODIFIED SF SOLVENTS

The solvatochromic parameters were developed for use in LSERs. The Linear Solvation Energy Relationship (LSER) can be represented (Yonker et al. 1986) by

$$XYZ = XYZ_0 + a\alpha + b\beta + s\pi^*, \quad (6)$$

where XYZ is a property dependent on the solvent (absorption maximum, solubility, etc.), α is a scale of solvent hydrogen-bond donor acidities, β is a scale of solvent hydrogen-bond acceptor acidities, and the term $s\pi^*$ is a measure of polarity and polarizability effects. This is a form of the generalized linear solvation energy relationship (Kamlet et al. 1983). Equations of this type have proven very useful in correlating and predicting effects dependent on solvent and supercritical solvents are no exception.

Hyatt (1984), in the course of the study summarized earlier in this review, examined the solvatochromic behavior of SF-CO₂. He reported that π^* was about -0.5 for SF-CO₂ and about -0.4 for

liquid CO₂, and pointed out that these were among the lowest π^* values known; fluorocarbons have π^* values in the range of -0.33 to -0.41 and hydrocarbons have $\pi^* = 0.00$ to -0.08, while nearly all other solvents have positive π^* values.

Sigman, Lindley, and Leffler (1985) studied the behavior of π^* and β for liquid CO₂ and SF-CO₂ of different densities, using a series of solvatochromic indicators; the indicators were a series of aromatic compounds whose ultraviolet spectra were used in evaluating the parameters. It was found that the values of π^* were strongly dependent on density, decreasing smoothly toward the value for vacuum (-1.0) as the density was decreased. The values of π^* for liquid CO₂ were found to be close to those for SF-CO₂ of the same density (0.80-0.82 gm/cm³). The hydrogen-bonding basicity parameters β for SF-CO₂, liquid CO₂, and vacuum are all near zero or slightly negative, suggesting only limited capacity for SF-CO₂ to function as a hydrogen-bond base.

Yonker et al. (1986) used the UV spectra of solvatochromic probe molecules to characterize the relative polarity-polarizability terms of supercritical NH₃, CO₂, N₂O, CCl₃F, and CO₂-methanol. The indicator (2-nitroanisole), solvents, etc., were chosen for this work to minimize hydrogen-bonding effects, so that equation (6) reduced to

$$v_{\max} = v_0 + s\pi^* \quad (7)$$

Again, the π^* values varied with reduced density.

Ikushima et al. (1991) studied the α , β , and π^* values for SF-CO₂ by infrared spectroscopy, using the carbonyl frequencies of cyclohexanone, acetone, and N,N-dimethylformamide. They found that the hydrogen-bonding parameters α and B_{MeOD} (a parameter proportional to β) were very small, and that π^* varied with density from -1.1 in vacuum to zero at a density of 0.85 gm/cm³. They also studied the $E_T(30)$ (a parameter related to polarization of solvent molecules) values for SF-CO₂.

Ikushima, Saito, and Arai (1993) studied the solvatochromic parameters for SF-CO₂ and systems involving SF-CO₂ combined with the cosolvent modifiers ethanol, 2,2,2-trifluoroethanol, and dimethyl sulfoxide. They found that the α , β , and π^* values were changed greatly by addition of the cosolvents, as were values for $\pi^{*'}$, a parameter defined by the equation

$$\pi^{*'} = \pi^* + (a/s)\alpha + (b/s)\beta, \quad (8)$$

where all quantities have the meanings assigned above. Results depended on pressure/density, but, in general, for the solvent-cosolvent systems, π^* and π^{**} became markedly positive (instead of negative as in the case of pure SF-CO₂), while α (for trifluoroethanol and ethanol only) rose from nearly zero to values as high as 0.7 and β (for ethanol and DMSO only) rose from nearly zero to values as high as 0.5. Thus addition of cosolvents to SF-CO₂ caused the combined system to take on higher solvatochromic-parameter values, values which at higher densities can approach those of the pure cosolvents.

O'Neill, Kruus, and Burk (1994) used 2-nitroanisole as a UV indicator; they studied the solvatochromic behavior of SF-CO₂ and SF-N₂O. It was found that the π^* values for SF-CO₂ and SF-N₂O became more positive or less negative with increasing density, in a manner similar to that described above. The solubilities of the polyaromatic hydrocarbons chrysene, anthracene, and *meta*-terphenyl qualitatively followed the trend in solvent power predicted by π^* ; however, the relative solvent powers of SF-CO₂ and SF-N₂O predicted on the basis of π^* followed an order opposite to that determined experimentally; nevertheless, it was suggested that the π^* parameter might be of some use for solubility predictions only a limited set of solute-solvent systems were considered. When tetrahydrofuran (THF) was added to SF-CO₂, π^* was increased by an amount up to about 0.1; solubilities were also increased.

The situation with regard to linear solvation energy parameters of SF-CO₂ can be summarized as follows: for unmodified SF-CO₂, the polarity-polarizability parameter π^* is density-dependent, but is very low, generally having a negative or low positive value, while the hydrogen-bonding parameters α and β for pure SF-CO₂ are very low or zero. However, it appears that addition of cosolvent can cause the combined system to take on values for these parameters that are density dependent, but may be closer to those characteristic of the cosolvent than to those characteristic of pure SF-CO₂.

The linear solvation energy approach seems capable of providing a basis for theoretical modelling of both solubility and cosolvent effects. Solubility itself could be modelled by an approach similar to that of Famini and Wilson (1993), in which the various linear solvation energy interactions for various solutes are represented by quantities calculated from molecular orbital or other theory, and then summed to obtain numbers representative of the solubilities of the solutes in a given solvent.

Cosolvent effects could possibly be modelled by initially attempting to treat them as a linear function of the composition of the solvent-cosolvent system, allowing the parameter values for the solvent-cosolvent

mixture to be linearly related to those for the solvent and cosolvent separately; if this proves to be an oversimplification, possibly some other form of monotonic relationship would give satisfactory results.

6. DISCUSSION, CONCLUSIONS, AND RECOMMENDATIONS

In this section, we will first briefly summarize the conclusions that can be drawn from the literature summarized herein, then attempt to explain the effects observed and make recommendations for future work in such areas as the identification of SF solvents for supercritical extraction of nitramines such as HMX and RDX, and the enhancement of their solubility in inexpensive, readily available solvents such as SF-CO₂.

6.1 Structure-Solubility Relationships. The relationship between solute molecular structure and solubility in SFs appears to be expressible in terms of certain general rules. These rules are most applicable to SF-CO₂, for which by far the most data is available, but similar trends appear to be followed in other solvents as well:

- (1) Increasing molecular size leads to decreased solubility. The lower members of many homologous series are completely miscible with, e.g., SF-CO₂, while solubility drops off for the higher members.
- (2) Among aliphatic compounds, branching or (this next may seem surprising in view of (3) below) the presence of double bonds leads to greater solubility.
- (3) In general, aromatic compounds tend to be less soluble than their hydrogenated counterparts.
- (4) In general, addition of substituents causes a decrease in solubility. This is especially true for strongly electron-withdrawing (such as nitro groups) or hydrogen-bonding substituents.
- (5) Esterification, etherification, alkylation, or acylation of protic groups such as hydroxy, amino, or carboxylic acid causes an increase in solubility.

- (6) The basicity of amines has a tremendous effect on their solubility in SF-CO₂, with the more basic amines, such as aliphatics, tending to react with CO₂ to form carbonates.
- (7) Of especial interest to the present work, nitro groups tend to decrease solubility, especially if more than one is present. The exact effect of chain length in nitroaliphatics has not been determined, but homologs up to nitropropane are fully miscible in SF-CO₂. Substituents have strong effects, most leading to a decrease in solubility.

6.2 Effect of Supercritical Solvent on Solubility. In general, in the supercritical regime as in the subcritical regime, a "like dissolves like" rule applies. The effect of supercritical solvent on solubility can be expressed in terms of the following general rules.

- (1) Hydrocarbons such as SF-ethane and SF-ethylene are good solvents for hydrocarbons; however, introduction of polar functional groups into the solute causes a decrease in solubility in hydrocarbon solvents.
- (2) Polar solvents such as SF-CHF₃ are good solvents for all substances except nonpolar hydrocarbons. The solubility of polar but nonassociated compounds are particularly high in these solvents.
- (3) SF-CO₂ is generally a fairly good solvent for most organic compounds. Electron-releasing substituents make SF-CO₂ a better solvent, while electron-withdrawing substituents reduce its dissolving power. While SF-CO₂ is generally thought of as being a "hydrocarbon-like" solvent, it possesses enough charge separation to enable it to dissolve the general run of organic compounds.

6.3 Relationship Between Molecular Structure and Cosolvent-Modifier Properties. As mentioned before, a cosolvent modifier is a compound, usually having a low molecular weight, which is added in small amounts (ca. 1-10%) to a supercritical solvent to improve the solubility of solutes that would otherwise be relatively insoluble in that solvent. The main rule that appears to operate with regard to cosolvent effects is that to have a strong solubility-enhancing cosolvent effect, there must be a specific interaction of some sort between the solute and the cosolvent. This interaction is most commonly one of

the following types: (a) hydrogen bonding, (b) charge transfer, or (c) dipole-dipole interaction. In the previous review, numerous cases are mentioned in which small increases in solubility result from addition of modifiers that do not seem offhand to be capable of specific interaction with the solute. Possibly these are explainable in terms of dispersion forces, or in terms of a dipole-orientation effect in which the cosolvent molecules, while interspersed among the solvent molecules, stabilize the dipole moment of the solute molecule in solution.

Possibly one way to discuss cosolvent effects in terms of structure-property relationships would be to relate the cosolvent effects to the solvatochromic parameters (see Section 5) for the modified solvents and for the difference in solvatochromic parameters between the modified and unmodified solvents.

6.4 Discussion of and Possible Approaches to Cosolvent Modification of SF-CO₂ to Facilitate Dissolution of Energetic Materials. In view of solubility rules (4) and (7) in Section 6.1, it is not surprising to find that, as discussed in Section 2, HMX and RDX have only poor solubility in SF-CO₂. A main thrust of research in this laboratory is to find "environmentally friendly" ways of recovering and recycling the ingredients in excess propellants and explosives. Furthermore, some explosives and propellants contain as much as 70–80% HMX or RDX; therefore, a prime goal is to find conditions for supercritical fluid extraction of RDX and HMX.

The solvents under consideration are CO₂, NH₃, CH₃F, and CHF₃; of these, CO₂ is the most interesting because of its low cost, availability, and environmental innocuousness. However, as mentioned before, HMX and RDX are not very soluble in CO₂. Therefore, we are attempting to find cosolvent modifiers that will enhance the solubilities of HMX and RDX in SF-CO₂. The discussion in the preceding paragraphs contains some clues as to how this problem might be approached. Clearly, the way to approach the problem is to look for molecules which are soluble in SF-CO₂ and which appear capable of engaging in some sort of specific molecular interaction with HMX and RDX; this interaction will presumably take place with the nitro portions of the nitramine groupings in HMX and RDX.

Specific interactions of the following types were mentioned above, as being capable of leading to cosolvent enhancement of solubility: (a) charge transfer, (b) hydrogen bonding, or (c) dipole-dipole interaction. First, nitro compounds appear to be capable of engaging in charge transfer interactions (Constantinou, Mukundan, and Chaudhri 1992) with amines, which contain lone pairs on their nitrogen atoms. Second, the lone pairs of electrons and the relatively high charges on the nitro oxygens of HMX

and RDX indicate that they should be capable of hydrogen bonding to such common proton donors as methanol and other alcohols. Finally, the relatively high nitro and nitramine group dipole moments of nitramines such as RDX indicate that dipole-dipole interactions with polar cosolvents should be possible. Thus, it appears that the nitro groups in HMX and RDX should be capable of engaging in all three of the forms of interaction mentioned above. This allows some suggestions as to possible cosolvents for use with SF-CO₂, and as to possible explanations for the effects already observed.

Examination of Table 1 indicates that the compounds that give the strongest cosolvent effects (nitromethane and acetonitrile) are also the ones with the largest dipole moments. This is consistent with the idea that, at least with regard to solubility of RDX in SF-CO₂, cosolvent effects are dominated by dipole-dipole interactions between the dipole moment of the cosolvent molecule and that of the RDX molecule, and that hydrogen bonding is of secondary importance, at least for hydrogen bonders no stronger than methanol, isopropanol or water. However, it is difficult to evaluate the possible role of electron-transfer interactions without more data than is contained in Table 1.

Even with acetonitrile or nitromethane as a cosolvent, the solubility of RDX in SF-CO₂ is not all that good (Table 1); possible methods for improving on these cosolvent effects include: (a) careful optimization of the cosolvent effect as a function of concentration, temperature, density/pressure, etc.; and (b) use of higher aliphatic nitriles and nitroaliphatic compounds such as propionitrile, butyronitrile, nitroethane, etc., in place of acetonitrile and nitromethane. This is based on analogy with the finding (for SFC) of Blilie and Greibrokk (1985) and of Ting et al. (1993a) that the cosolvent effects of alcohols increased with the length of the carbon chain in the alcohol molecule.

One way to check for the influence of electron-transfer reactions might be to use, as cosolvents, compounds with different types of lone pairs on nitrogen. Possible candidate compounds include pyridine and other azabenzene or azole (azapyrrole) heterocyclic compounds, and simple aromatic amines such as aniline. (Use of simple aliphatic amines could also be considered, but would probably be limited by the tendency of many such amines to react with CO₂ [see, for example, Dandge, Heller, and Wilson (1985)] and [Rule 6 in Section 6.1]).

The relatively weak (6.6-fold), but not negligible, cosolvent effect observed for methanol (Morris et al. 1993) on the solubility of RDX in SF-CO₂ is probably attributable to hydrogen bonding between the hydroxyl group of methanol and the nitro oxygens of RDX.

In addition to careful optimization of the cosolvent effect as a function of temperature, density/pressure, cosolvent concentration, etc., this could possibly be improved on by replacing methanol by an alcohol-containing, electron-withdrawing substituent groups. For example, Ekart et al. (1993) found that 2,2,2-trifluoroethanol exhibited a considerably stronger cosolvent effect than ethanol or isopropanol, especially toward solutes capable of acting as hydrogen-bond receptors. This was attributed to the greater ability of the hydroxyl group of 2,2,2-trifluoroethanol to donate a proton in a hydrogen-bonding situation. Note that the solvent in this case was SF₆-ethane; however, the nitro oxygens of RDX should be sufficiently strong hydrogen-bonding proton-acceptors that it does not seem unreasonable to suggest that a similar effect might operate in SF₆-CO₂. Another possible way to improve on the cosolvent effect of methanol might be use of higher aliphatic alcohols such as n-propanol, n-hexylalcohol, etc., in place of methanol. As above, this suggestion is based on analogy with the findings of Blilie and Greibrokk (1985) and of Ting et al. (1993a) that the cosolvent effects of alcohols in SFC increased with the length of the carbon chain up to six carbon atoms.

Another possible way of improving on the cosolvent effect of methanol might be to use a more strongly hydrogen-bonding class of hydroxyl-group-containing compounds such as carboxylic acids. Another possibility might be to use a heterocyclic nitrogen compound capable of hydrogen bonding, such as pyrrole or one of the higher azoles such as pyrazole, imidazole, or one of the triazoles. These higher azoles have, in addition to their hydrogen-bonding NH groupings, pyridine-type nitrogen atoms which may well be capable of undergoing electron-transfer with the nitro groups of HMX and RDX; the possibility that this dual effect might lead to improved cosolvent properties for these compounds should be examined. Possibly, the hydrogen-bonding would not reduce the solubility sufficiently to preclude use of these types of compounds as modifiers at concentrations of about 1 to 10%.

Another possible way to select possible cosolvents would be by the use of theoretical calculations of the kinds described in Section 3.3. However, as far as the author is aware, there are as yet no theoretical calculations at the molecular level (e.g., molecular orbital calculations) which address the topic of cosolvent (as opposed to solubility) effects.

A number of calculated and experimental molecular properties could possibly be used as molecular indices in order to estimate the strength of the various components of the cosolvent effect.

The importance of the dipole-dipole interaction component of the cosolvent effect could possibly be gauged from calculated or experimental dipole moments; in general, a high dipole moment should indicate a greater tendency to interact electrostatically with the high dipole moment of a solute such as RDX. It should be noted, however, that steric factors might cause molecules of different shapes to interact with solute in different ways.

The importance of the hydrogen-bonding component of the cosolvent effect could possibly be gauged by calculating energy differences between hydrogen-bonded complexes and the isolated molecules of the components that make up the complex. Another possible type of index might be the charge on a hydrogen atom, or on a nitrogen or oxygen atom or lone pair that might act as receptor for a hydrogen bond. As above, it should be noted that steric factors might cause molecules of different shapes to interact with solute in different ways. Two possibly related experimental indices of hydrogen-bonding ability of cosolvent molecules might be the solvatochromic parameters (Kamlet et al. 1983) α and β of the candidate cosolvents when used as solvents; α is a measure of the ability of a solvent to donate a proton in a hydrogen bond and β is a measure of the ability of the solvent to accept a proton (donate an electron pair) in a hydrogen bond. (Values for α and β parameters are tabulated in the literature; see for example Kamlet et al. [1983].)

Possible indices of the electron-transfer component of the cosolvent might be calculated energy differences between the sum of the neutral solute and cosolvent molecules on the one hand, and cation and anion radical pairs formed by electron transfer on the other. Alternative indices, possibly easier and faster to obtain, might be the energies of the highest (higher energy suggests stronger cosolvent effect by that molecule with an appropriate solute, such as RDX) occupied molecular orbital (HOMO) of the electron-donor molecule and/or the lowest (lower energy suggests stronger cosolvent effect by that molecule with an appropriate solute) unoccupied molecular orbital (LUMO) of the electron-receiving molecule.

In all cases discussed in the preceding three paragraphs, the approach employed would be to calculate, for an isolated molecule, by a molecular orbital method, the quantity being used as an index of cosolvent effect. This would then be repeated for a series of molecules that are structurally related to the first. The compound which gives the optimal value of the index being used would be the one in which that component of the cosolvent effect is strongest. Note that in order to optimize the total cosolvent effect for a particular solute, it may be necessary to consider two or more components.

Another more complete approach to the modeling or quantitative estimation of cosolvent effects could possibly be carried out as suggested in Section 5. Solubility itself could be modeled by an approach similar to that of Famini and Wilson (1993), in which the various linear solvation energy interactions for solvent and solute are represented by quantities calculated from molecular orbital or other theory, and then summed to obtain numbers representative of the solubilities of the solutes in a given solvent.

It was mentioned before that Ikushima, Saito, and Arai (1993) found that solvatochromic parameters for solvent-cosolvent systems tend to take on values resembling those of the cosolvents. Based on this finding, cosolvent effects could possibly be modeled by initially attempting to treat them as a linear function of the composition of the solvent-cosolvent system, allowing the parameter values for the solvent-cosolvent mixture to be linearly related to those for the solvent and cosolvent separately. If this proves to be an oversimplification, possibly some other form of monotonic relationship would give satisfactory results.

Molecular workstations now available may make it possible to calculate such effects with inclusion of both solute and cosolvent molecules, as well as a number of solvent molecules. Possibly, the total cosolvent effect could be modeled by just allowing such a system to optimize until an energy minimum is reached, then repeating for a succession of different candidate cosolvent molecules with the solute of interest, e.g., RDX.

The next question that arises is "What should be tried if it proves impossible to modify SF-CO₂ sufficiently to get satisfactory solubility for RDX and HMX?" One possibility, especially in view of the polarity of RDX and HMX and of solubility rule (2) in Section 6.2, might be to try a more polar solvent, such as SF-CF₃H. If SF-fluoroform alone is an insufficiently strong solvent, possibly the use of the same cosolvents (e.g., acetonitrile, nitromethane), that have improved the solubility of HMX and RDX in SF-CO₂ would improve their solubility in SF-CF₃H.

Another possibility is the use of supercritical xenon as a solvent for SFE. The critical properties of SF-Xe are similar to those of SF-CO₂, and its solvating properties are about the same as, and in some cases better than, those of SF-CO₂ (Krukoni, McHugh, and Seckner 1984; Jenkins et al. 1992). The improved solvating properties of SF-Xe are presumably due to the fact that it has a greater atomic radius than and is consequently more polarizable than the atoms in the other solvents that we have been discussing. Since RDX and HMX are unusually polar molecules, the solvating power of Xenon should

be especially good for them. Xenon is quite expensive, but if it were recycled within a closed system, it may not be unreasonable to hope that, once start-up had been achieved, xenon losses could be kept low enough to keep costs within reasonable bounds. SF-Xe could presumably be modified with cosolvents, in a manner similar to the other supercritical solvents considered here.

Finally, in view of its known ability to dissolve HMX and RDX (see Section 2), SF-ammonia could always be used. However, in view of the toxicity and odor of gaseous ammonia, it seems worth considerable effort to develop alternatives involving materials such as cosolvent-modified SF-CO₂, cosolvent-modified SF-CHF₃, or SF-xenon.

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EPILOGUE

Section 6 contains a number of suggestions for additional work. Since it was written, a number of these have been addressed. Morris et al.^{1,2} examined the use of 36 organic compounds, containing an assortment of functional groupings, as cosolvent modifiers for solubility of RDX in SF-CO₂. The most interesting correlations noted were that (a) a large (\geq ca 3.5 D) dipole moment was a necessary but not sufficient condition for a large cosolvent effect; (b) with the exception of acetonitrile, a molar mass of at least 70 seemed to be a necessary but not sufficient criterion for a large enhancement factor; (c) in general, modifiers having electron-withdrawing substituents tended to be more effective; and (d) there was a general correlation between extraction enhancement by a given modifier and solubility of RDX in that modifier when used as a solvent for RDX. For further results and discussion of this work, see Morris et al.^{1,2}

Important progress has been made, as described previously, but there are still a number of areas in which further research is needed before it will be possible to intelligently design cosolvent modifiers for extraction of specific energetic materials such as HMX and RDX with SF-CO₂.

First, examination of the paper referred to previously suggests that there is only limited understanding of the underlying reasons behind the observed trends.^{1,2} Dipole moment and polarizability of the modifier molecule seem to be important, judging from the observed threshold values for dipole moment and molecular mass (used as an approximate gauge of polarizability). Furthermore, hydrogen bonding seems to be less important. However, it is difficult to evaluate the role of charge transfer on the basis of the available information.

Although some data exist, there is a need for more information on the effect of the electron-withdrawing power of a substituent on the modifier effectiveness of the molecule of which it is a part. Such information could be obtained by studying the variation in cosolvent effects along several series of molecules containing the same hydrocarbon portion (i.e., methyl, ethyl, phenyl), but with substituents of

¹ Morris, J. B., M. A. Schroeder, R. A. Pesce-Rodriguez, K. L. McNesby, and R. A. Fifer. "Supercritical Fluid Extraction and Recovery of Nitramine Energetic Materials From Large Caliber Gun Propellant." Presented at and to appear in the proceedings of the "Life Cycles of Energetic Materials" conference, Del Mar, CA, December 1994.

² Morris, J. B., M. A. Schroeder, R. A. Pesce-Rodriguez, K. L. McNesby, and R. A. Fifer. "Supercritical Fluid Extraction of Nitramine-Based Gun Propellant: A Fluid Study." To be published.

molecules containing the same hydrocarbon portion (i.e., methyl, ethyl, phenyl), but with substituents of differing electron-withdrawing capabilities, ranging from strongly electron donating through neutral to strongly electron-withdrawing. There is also a need for further information on the effect of the structure of the alkyl or aromatic portion of a modifier on its effectiveness; this could be obtained from studies on the modifying abilities of several series of modifiers, each series having the same substituent (e.g., nitrile, nitro, hydroxy, etc.) and a systematically varied hydrocarbon portion (e.g., methyl, ethyl, 1-propyl, etc.).

Another possible way to select possible cosolvents would be by the use of theoretical calculations of the kinds described earlier in the present writeup for isolated molecules. However, as far as the present writer is aware, there are as yet no theoretical calculations at the molecular level (e.g., molecular orbital calculations) which address the topic of cosolvent (as opposed to solubility) effects. A number of calculated and experimentally-determined molecular properties could possibly be used as molecular indices or parameters in order to estimate the strength of the various components of the cosolvent effect. Some examples include use of calculated charge distributions or energies of hydrogen bonding as indices of the extent of hydrogen bonding, or of calculated orbital energies as indices of charge-transfer contributions to cosolvent effect.

It was mentioned previously that Ikushima, Saito, and Arai³ found that solvatochromic parameters for solvent-cosolvent systems tend to take on values resembling those of the cosolvents. Based on this, cosolvent effects could possibly be modelled by initially attempting to treat them as a linear function of the composition of the solvent-cosolvent system, allowing the parameter values for the solvent-cosolvent mixture to be linearly related to those for the solvent and cosolvent separately. Parameter values could possibly be estimated using methods similar to those of Famini and Wilson.⁴ If this proves to be an oversimplification, possibly some other form of monotonic relationship would give satisfactory results.

Molecular modeling software now available may make it possible to calculate such effects with inclusion of both solute and cosolvent molecules, as well as a number of solvent molecules. It is possible that the total cosolvent effect could be modeled by just allowing such a system to optimize until an energy minimum is reached, then repeating for a succession of different candidate cosolvent molecules with the solute of interest (e.g., RDX).

³ Ikushima, Y., N. Saito, and M. Arai. "Measurement and Linear Correlation of the Solvent Polarity Parameters of Supercritical Carbon Dioxide and its Cosolvent Systems." Bulletin of the Chemical Society of Japan, vol. 66, pp. 1817-1819, 1993.

⁴ Famini, G. R., and L. Y. Wilson. "Using Theoretical Descriptors in Structure-Activity Relationships: Solubility in Supercritical CO₂." J. Phys. Org. Chem., vol. 6, pp. 539-544, 1993.

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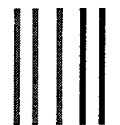
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